PHASE RULE

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PHASE RULE

INTRODUCTION

- **"Phase rule"** is an important tool used for the quantitative treartment of systems in equilibrium.

- It enables us to predict the conditions that must be specified for a system to exhibit equilibrium.

- Two or more different phases are present in equilibrium to form a **"heterogenous system"**. Such system are studied by phase rule.

- J. Willard Gibbs enunciated the phase rule in 1876 on the basis of Thermodynamic principles

- This rule predicts qualitatively the **effect of temperature, pressure and concentration** on a heterogenous equilibrium.

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Gibbs phase rule

“ In a heterogeneous system in equilibrium is not affected by gravity or by electrical and magnetic forces, the number of degrees of freedom(F) of the system is related to the number of component(C) and the number of phases(P) existing at equilibrium”.

It is expressed by mathematically,

$$F = C - P + 2$$

where,

F - number of degrees of freedom
C - number of components
P - number of phases
2 - additional variables of temperature and pressure

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Phase

It is defined as **“ Physically distinct, homogenous and mechanically separable part of a system ”.**

(i) A gaseous mixture constitutes a single phase since gases are completely miscible.

example : **Air**

(ii) Two or more liquids which are miscible with one another constitute a single phase as there is no bounding surfaces separating the different liquids.

example : **water and alcohol**, **chloroform and benzene** constitute one phase system.

(iii) A system consisting of a liquid in equilibrium with its vapour constitute a two phase system

example : $H_2O_{(l)} \rightleftharpoons H_2O_{(g)}$

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Component

It is defined as "Minimum number of independent variable constituents which are required to express the composition of each phase in the system".

In a chemically reactive system, the number of components is given by

$$C = N - E$$

Where, C - components.

N - Number of chemical species

E - Number of independent equations relating to the concentrations of the species.

- Each independent chemical equilibrium involving the constituents count as one equation.
- The condition that a solution be electrically neutral also counts as one equation if ions are considered as constituents.

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Examples

(i)Sulphur system

(a)monoclinic sulphur, (b)rhombic sulphur (c)liquid sulphur (d) sulphur vapour. **(C = 1; P=4)**

(ii) Water system

solid,liquid and vapour
(C=1 ; P = 3)

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(iii) Salt + water system

- Certain salts are capable of existing as hydrates with different number of water molecules of crystallization.
  The system is a two component.**(C=2 , P = 1)**

- The composition of each phase of the hydrates is completely described in terms of the anhydrous salt and water alone. e.g., **Na_2SO_4 + water**

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Degrees of Freedom

"It is defined as the minimum number of independent variables such as temperature, pressure and concentration which should be specified in order to define the system completely".

Examples

(i)State of a pure gas can be specified by two variables P and T or P and V , third variable can be calculated.
Hence pure gas has degree of freedom two (F = 2)

(ii) $H_2O_{(l)} \rightleftharpoons H_2O_{(g)}$ (F = 1) **Monovariant**

(ii) A gaseous mixture say N_2 and O_2 gases is completely defined when three variables(T,P and C).

(F=3) **Trivariant.**

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(i)The greater the number of components in a system, greater is the degree of freedom for a given number of phases.

(ii) The greater the number of phases, the smaller is the number of degrees of freedom.

(iii) The number of phases is maximum, the number of degrees of freedom = Zero, for a given number of components.

For

One component system P = 3

Two component system P = 4

Three component system P= 5

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Advantages

(i) It provides a simple method of classifying **equilibrium states of systems.**

(ii) The phase rule confirms that the different systems having the same **number of degrees of freedom** behave in same manner.

(iii) It is applicable only to **macroscopic systems** and not concerned with molecular structure.

(iv) It predicts the **behaviour of the systems** with changes in the variables that govern the system in equilibrium.

(v) It predicts that, under a given conditions whether a number of substances taken together would **remain in equilibrium** or it involves in some **interconversion or elimination.**

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(vi) It does not give the informations about the nature of the reactants or products in the reactions

(vii) It finds extensive use in the study of many heterogeneous systems.

(viii) It is extremely useful in the extraction of metals.

Limitations

(i) The phase rule is **applicable to heterogeneous systems in equilibrium**, hence it is not applicable for the **systems which are slow** to attain the equilibrium state.

(ii) It is applicable to a **single equilibrium state.** It never gives information about the other possible equilibrium in the system.

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(iii) Variables such as **temperature, pressure and composition** are only taken into account in Gibbs phase rule, .

(iv) It does not take in account the **electric and magnetic influences**. For consideration of such variables, the factor 2 of the Phase rule has to be adjusted accordingly.

(v) All the phases in the system must be present under the **same Temperature, Pressure and Gravitational force .**

(vi) Solid or liquid phases are not finely divided, If it happens deviation must occurs.

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Phase diagrams

A phase diagram is a type of chart used to show condition (pressure, temperature, concentration, etc) at which thermodynamically distinct phases (such as solid, liquid or gaseous states) occur and coexist at equilibrium

- The number of phases that exist in equilibrium depends upon the conditions of **temperature and pressure** or **temperature and composition**, pressure being constant.

- These conditions are determined experimentally and the values of the variables can be exposed graphically by using appropriates coordinates. These diagrams are called **phase diagram.**

- It is very easy to describe the **phase behaviour of a system** by such diagrams and to investigate the conditions in which various phases will constitute the system .

phase diagram does not plot on the scale, it show only important conditions when one phase changes to another phase

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Application of Gibbs Phase Rule

One Component System

From the mathematical expression of phase rule,

$$F = C - P + 2$$

When C = 1, P = 1

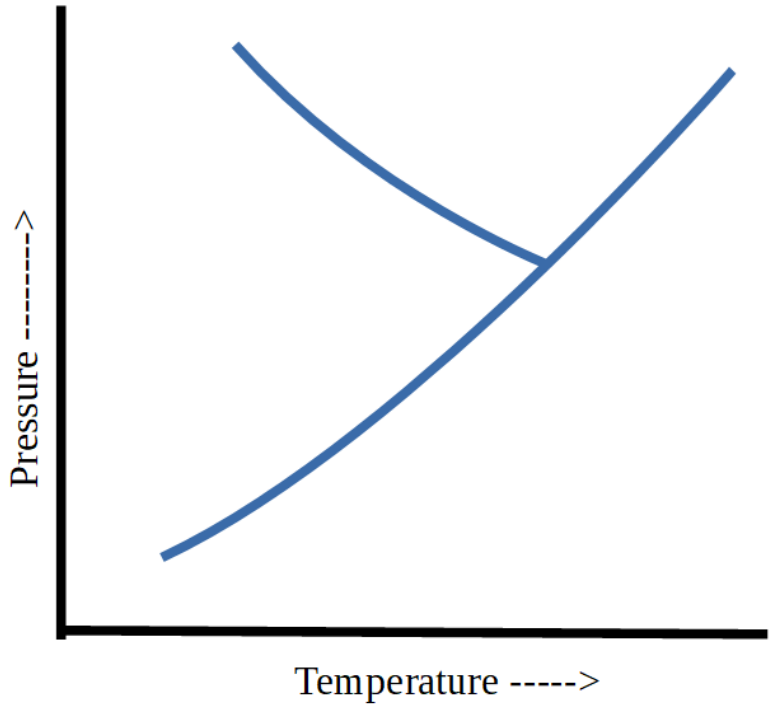
$$F = 1-1+2$$

$$= 2$$

All one component systems can be completely described graphically by stating only two variables such as **pressure and temperature** on appropriate axis.

Typical phase diagram of one component system

it plots between pressure and temperature on the ‘x’ axis and pressure on the ‘y’ axis so it is called (P-T) graph. For one component system concentration is constant because only one component is present.



In phase diagram, curves (lines), area (between two curves) and point (where two or more lines are meet) are present

Name of curves

1. sublimation curves

solid $\rightleftharpoons$ gas

2. fusion curve

solid $\rightleftharpoons$ liquid

3. vaporisation curve

liquid $\rightleftharpoons$ vapour

4. transition curve

solid(A) $\rightleftharpoons$ solid(B)

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Water System

- It is a one component system.(H_2O)
- Water exists in three possible phases viz. ice (solid) , water (liquid), and vapour (gas). These three single phases may form four possible equilibria.

(i) Solid $\rightleftharpoons$ Liquid

(ii) Liquid $\rightleftharpoons$ Vapour

(iii) Solid $\rightleftharpoons$ Vapour

(iv) Solid $\rightleftharpoons$ Liquid $\rightleftharpoons$ Vapour

To draw a phase diagram of water system we have some information about this system

1. m.p. of water = 0°C at 1atm

2. b.p. of water = 100°C at 1atm

3. density of ice < water

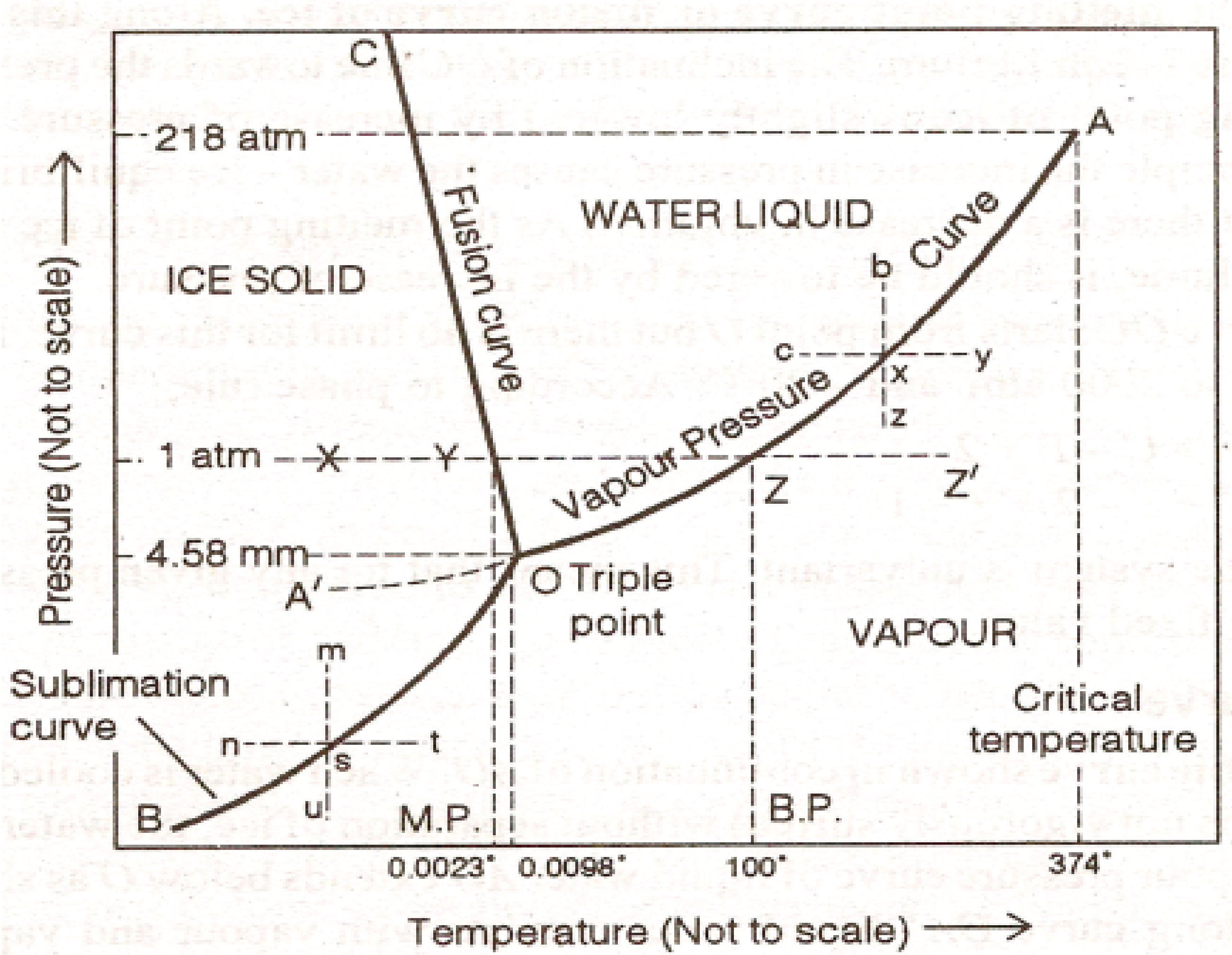
4. b.p. of water increases with pressure

5. m.p. of ice decreases with increasing pressure

6. All three phases, ice, water, water vapour present only at 4.58mm pressure and 0.0098°C

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Phase Diagram of water system



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The phase diagram consists of the following important aspects

(i) **Stable curves:** three *OB*, *OA* and *OC*

(ii) **Metastable curve:** one OA'

(iii) **Areas:** three AOB, COB and AOC

(iv) **Triple point:** One O

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Curve OA

(i)It is known as **vapour pressure curve of water**. The curve OA starts from point O i.e., freezing point of water, 0.0098°C under 4.579 mm of Hg pressure and ends at A, the critical temperature (374^{0}C at 218 atm.).

In This Curve 2 phases water and water vapour present in equilibrium

Water ⇌ Water Vapour

Phase (P) = 2 , component (C)=1

From phase rule, $F = C – P + 2$

$= 1- 2 + 2 \quad = 1$

The water vapour system is **univariant**

Effect Of Pressure on Boiling Point of Water

(i) Above critical temperature on the vapour phase exists whatever may be the value of pressure.

.(ii) The vapour pressure of water increases with increase in T

(iii) curve OA slants upwards and slopes away from the temperature axis.

Slope of OA Curve is away from pressure axis which shows that when we increase pressure b.p. of water also increases

b.p. of water at 1atm = 100°C
b.p. of water at 218 atm = 374°C

According to Le Chatelier's principle "Increase in pressure causes the water – water vapour equilibrium to shift in such a direction that their is a decrease in volume"

Because volume of water is less than volume of water vapour so when we increase pressure b.p. of water also increases

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Curve OB

(i) It is the **sublimation curve.** Along this curve, solid ice is in equilibrium with its vapour.

(ii) This curve is not the **prolongation of curve** A but falls of more steeply. Curve OB starts From the temperature 0.0098°C above which solid water *i.e.,* ice cannot exist.

(iii) The curve ends at *B* .It is present in **absolute zero (- 273°C).** At this temperature, no vapour can exist and, hence only the solid water(ice) is present.

(iv) The other points of the curve O*B,* ice is in equilibrium with vapour.

Ice ⇌ water vapour

Hence, there are two phases. According to phase rule,

$$F = C - P + 2$$
$$= 1 - 2 + 2 = 1$$

hence, the system **is univariant.**

This means that for **each temperature**; there may be **one pressure** and vice versa.

Curve OC

It is the **Melting point curve or Fusion curve of ice.** Along this curve two phases, ice and water are in equilibrium.

Ice ⇌ Water

According to phase rule,

F = C – P + 2 =1-2+2 = 1 (univariant)
(pressure and melting point have fixed value)

Effect of Pressure on Melting Point of Ice

The curve *OC* starts from point O but there is no limit for this curve. It goes upto a point corresponding to 2000 atm.

The inclination of OC line towards the pressure axis indicates that the melting point of ice is slightly lowered by increase of pressure.

Le Chatelier's principle states **that "Increase in pressure causes the water - ice equilibrium to shift in such a direction that there is a decrease in volume".**

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Metastable Curve

Curve OA′

(i) It is called **"metastable curve"** shown in continuation *of AO*. When water is cooled below its freezing point without separation of ice.

(ii) The water is said to be **"super cooled water"**. The vapour pressure curve of liquid water *AO* extends below O as shown by the dotted curve *OA′*.

(iii) Along curve *OA′* liquid water coexists with vapour. The vapour pressures are different than over the solid.

(iv) This equilibrium is called **"metastable equilibrium"** as slight disturbance brings it to the stable region *OB* of the phase diagram.

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Triple point O

- The point O at which the curves *AO, BO* and *CO* meet is called the "Triple point".

- At this point all the three phases *viz* , ice, water and vapour co-exist.

  Ice ⇌ Water ⇌ Water Vapour

  Thus, **P =3.**

  F = C –P + 2, =1-3+2 , **F = 0**

- It indicates that there is **only one set of variables P and T** at which all the three phases coexist.

- If any of the variables is changed, then the **number of phases decreases.**

- If the temperature is raised, the heat melts the soild ice.

- There is no change in temperature or pressure of the system occurs till the entire solid has completely converted into liquid.

- If it happens the system becomes a **two phase system (P = 2)**

we have learn that freezing point of pure water is 0°C at 1 atm pressure
here freezing point of water is 0.0098°C its reason are:-

1. In this phase diagram air free water is used. In daily life we use water which freezes at 0°C is not free from air i.e. it is behaves as solution (solvent pure water, solute=air), due to depression in freezing point its freezing point decreases by 0.0075°C

2. When we decreases pressure freezing point of ice increases
1atm = 76cm=760mm

Here freezing point recorded at 4.58mm pressure almost equal to – 1atm pressure so freezing point increases by 0.0023°C
that is why temperature of triple point of water is 0.0098°C (0.0075°C + 0.0023°C = 0.0098°C)

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Areas

(i) **BOC** - In this area only one phase ice is present

P=1, C=1

According to Phase Rule $F = C – P + 2$

$F = 1 - 1 + 2 = 2$

That means Area has 2 degree of Freedom Pressure & Temperature.

To Define any point in this area we required value of temperature and pressure both,

it is bivariant.

(ii) **AOC** – In this area only one phase water is present

it is bivariant

(iii) **BOA** – In this area only one phase water vapour is present

It is bivariant

Thank you